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AUTHOR(S):

Ishibashi, Masayoshi; Fujinaga, Taitiro; Sinozuka, Huziko

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The Use of Metal Oxide Electrode of High Positive Potential and its Application to the Determination of Chromate and Vanadate with Ferrous Iron

Masayoshi ISHIBASHI, Taitiro FUJINAGA and Huziko SINOZUKA*

(Ishibashi Laboratory)

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In this paper, the amperometric titration of chromate and vanadate with ferrous iron is reported; the rotating platinum indicator electrode was maintained at 1.07 volts vs. S. C. E. by short-circuiting with the opposit cathode made of manganese dioxide, and no e. m. f. needed to be applied to the cell. This method is believed to be one of the simplest electrometric methods and the result of determination was quite satisfactory.

INTRODUCTION

Kolthoff and May¹⁾ reported on the amperometric titration of chromate with ferrous iron and the method was accurate within 0.5 % at concentration as small as 10^{-4} M. The method was applied by Parks²⁾ to the determination of chromium and vanadium in steel. In these titrations, the rotating platinum wire micro-electrode was maintained at 1.0 volt vs. the saturated calomel electrode using the external e. m. f. or a battery and a potentiometer.

The authors³⁾ have, on the other hand, reported that many sorts of amperometric titrations can be performed by the short-circuit method in which the outside e. m. f. to obtain the cathodic diffusion current was substituted by high negative potential electrode such as zinc amalgam (its potential is -1.12 volts vs. S. C. E.) and in many practical titrations these non polarizable electrodes had proved to be usable as well as the outside e. m. f. method.

In this paper, for the non polarizable positive electrode to measure the anodic diffusion current, the metal oxide-metal ion system is taken into accounts (or a reversible electrode as ceric-cerrous equilibrium would also be applicable to this purpose). Among these, the manganese dioxide-manganous system is expected to be the most suitable for the reductometric titration with ferrous iron. Actually, in comparing with other electrodes, manganese dioxide electrode was found to be the most adequate to this titration in respects to the preparation, the preservation, the treatment and especially the potential (the normal potential of this system is 1.35 volts vs. N. H. E.).

* 石橋雅義・藤永太一郎・篠塚富士子

Hence the investigation with this electrode was examined as follows.

EXPERIMENTAL

Reagents

Ferrous standard solution: 0.01N-ferrous standard solution was prepared by dissolving Mohr's salt $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ in 2N-sulfuric acid.

Chromate and Vanadate standard solution: 0.01N-standard dichromate and ammonium vanadate solutions, in 0.1-sulfuric acid were prepared and their concentrations were determined with ferrous standard solution using diphenylamine as an indicator.

MnO_2 -electrode: it was electrolytically prepared according to the Matsuno's method; both platinum electrodes were immersed into the electrolysis solution consisting of 1.6 M- MnSO_4 , 0.4 N- H_2SO_4 , and 0.3 g- NaF/l and electrolysis was carried on at the voltage of 2V, the current density of about $1\text{A}/\text{dm}^2$ and the temperature of 85°C . By this method, fine γ - MnO_2 was deposited onto the platinum anode (in this experiment, platinum spiral of 20 cm in length and 1 mm in diameter was used). After sufficient electrolysis, it was cleaned up in hot water (the deposited MnO_2 must not be dried).

Apparatus

Figure 1 shows the total scheme of the titration apparatus: RE is a rotating

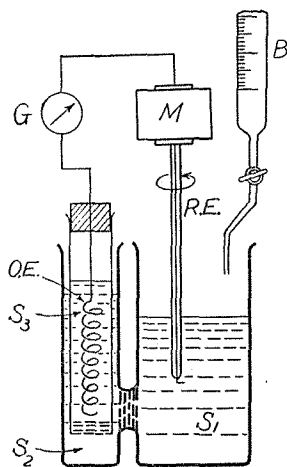


Fig. 1

platinum electrode, S_1 and S_2 are the anode and cathode compartments of H type cell separated with a sintered glass disk. The MnO_2 half-cell which is consisted of the tube filter of about 1 cm in diameter provided with a fine sintered glass disk at its end, the MnO_2 platinum spiral electrode OE and the catholyte S_3 consisting of 1 N- H_2SO_4 and 1 N- MnSO_4 are immersed into the cathode compartment filled with 1 N- H_2SO_4 .

To complete the circuit, the rotating electrode and the MnO_2 half-cell are short-

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circuited through a micro-ammeter G ($10-50\mu\text{A}$ in full scale).

Procedure

A sample of chromate or vanadate solution is taken into the anode compartment in the H-type electrolysis cell, and it is diluted to 50–100 ml with 1N- H_2SO_4 solution, then the rotating platinum electrode is inserted. The MnO_2 -electrode is put into the cathode compartment filled with 1 N- H_2SO_4 solution.

The current which flows through the cell is only residual current in the original chromate (or vanadate) solution. After the addition of 0.2ml ferrous standard solution from a microburette, the corresponding current is read on a microammeter.

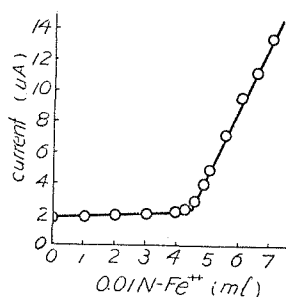


Fig. 2

These readings are made after successive addition of ferrous solution and the curve of current versus volume of ferrous solution is drawn as in Figure 2. The end-point is found graphically as the point of intersection of two lines, i.e., residual current line that is almost constant and anodic diffusion current line that is proportional to concentration of the excess ferrous ions.

RESULTS

Electrode Potential of Manganese Dioxide and its Stability

The potential of MnO_2 half-cell prepared as mentioned above keeps a constant value, 1.07 V vs. S. C. E., in the long use.

For instance, this MnO_2 half-cell was combined with calomel half-cell and they were short circuited through resistor of $30\text{ k}\Omega$ and constant electrolytic current of $32.5\mu\text{A}$ flowed continuously for 3 hours. The potential drop of MnO_2 half-cell with this experiment was only 6 mV as is shown in Table 1. The drop was almost recovered within several seconds after the circuit is opened and was kept constant for 30 days in despite of its frequent use.

Table 1. Change of the electrode potential of manganese dioxide with time.

Time	Electrolytic current	Electrode potential (vs. S. C. E.)
0 min.	0 μA	1.0722 volt
0 "	32.5	1.0693
5 "	"	1.0688
10 "	"	1.0688
20 "	"	1.0687
40 "	"	1.0682
90 "	"	1.0677
180 "	"	1.0665
180 "	0	1.0701
30 days	"	1.0693

Determination of Chromium and Vanadium

The result of the determinations of potassium dichromate solution and ammonium vanadate solution according to the prescribed method was shown in Table 2.

Table 2. Titration of chromate and vanadate with ferrous iron.

Metal taken	0.0117N-Fe ⁺⁺ used	Metal found	Error
Cr = 0.364 mg	1.79 ml	Cr = 0.361 mg	-0.95 %
0.910	4.43	0.902	-0.95
1.820	8.81	1.786	-1.90
V = 1.05 mg	1.76 ml	1.05 mg	0 %
2.62	4.36	2.60	-0.98
5.25	8.69	5.20	-0.98

CONCLUSION

In the amperometric titration with ferrous iron, MnO₂ half-cell was used as a cathode, and the rotating platinum electrode as an indicator anode, and no outside e. m. f. needed to be applied to the cell. Accordingly, it is said that this is the simplest electrometric titration method. And MnO₂ half-cell was stable for long time, and the result of the determination was satisfactory.

Similarly, ceric-electrode (1.2 V vs. S. C. E.), PbO₂-electrode (1.2 V), HgSO₄-electrode (0.45 V) etc. can be selected, in case of need, as a positive potential cathode.

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